Solubility of NH_4VO_3 in Water + Ammonia

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The solubility of NH_4VO_3 in water + ammonia in the temperature range of 293 K to 323 K has been studied. From these results a section of the solubility curve for the $NH_4VO_3 + NH_3 + H_2O$ system has been determined as well as the solution density dependence on the NH_3 concentration.

Introduction

Investigations on the utilization of $NaVO_3$ for the production of sodium carbonate by a method similar to Solvay's process according to the American patent (U.S. patent, 1967) have been undertaken. Application of this method requires knowledge of the equilibrium diagram for the $NaVO_3 + NH_4HCO_3 + H_2O$ system, as well as the solubility of $NaVO_3$ in water + ammonia as a function of temperature.

Trypuć and Kiełkowska recently reported the results of the equilibrium studies in $NaVO_3 + NaHCO_3 + H_2O$ (1995) and $NH_4HCO_3 + NH_4VO_3 + H_2O$ (1996) systems. According to Janecki, knowledge of the mutual solubility in these ternary systems is required to construct the equilibrium diagram of the five-component system $NaVO_3 + NH_4HCO_3 + NH_4VO_3 + NaHCO_3 + H_2O$ (Wiktorow, 1975).

On the basis of this diagram, it is possible to determine absolute values of the $NaVO_3$ and NH_3 concentrations in the given salt system for any assumed yield of the carbonization process with regard to the ammonium ion. Referring to the carbonization process of the solution $NaVO_3$ + ammonia + water, it has been stated (U.S. patent, 1967) that NH_4VO_3 precipitates whereas $NaHCO_3$ passes to the solution. In the classical Solvay method (Niederliński et al., 1978) as a result of the carbonization of NaCl + ammonia + water, $NaHCO_3$ precipitates whereas NH_4Cl remains in the solution.

Since the determined absolute values for the concentration of $NaVO_3$ and NH_3 in the investigated system do not refer to the exact solution composition in water + ammonia it seemed necessary to study the solubility of $NaVO_3$ in water + ammonia and its temperature dependence, as there appears to be no literature data on the given system.

The authors of this paper have undertaken investigations on the solubility of $NaVO_3$ in water + ammonia and have revealed already in the preliminary lab tests a reaction taking place in the given system, during which NH_4VO_3 precipitates. The amount of NH_4VO_3 in the solid phase, as referred to that of $NaVO_3$, is limited to the initial NH_3 concentration and temperature. This effect has not been observed while investigating many salt solubilities in water + ammonia, e.g., $NaCl + NH_3 + H_2O$ (Trypuć, 1987), $KCl + NH_3 + H_2O$ (Koneczny et al., 1973), and $KNO_3 + NH_3 + H_2O$ (Lango, 1971).

Only some fragmentary literature data can be found on the solubility of NH_4VO_3 in water + ammonia, for two temperature points, 291 K and 298 K, for the NH_3 concentration below 0.6 mol/dm^3 (Pelsh, 1969). It seemed necessary to study at first the solubility of NH_4VO_3 in water + ammonia as a function of temperature.

The given ranges of NH_3 concentrations and temperatures have been chosen on the basis of the operating parameters of Solvay's process of producing sodium carbonate (Niederliński et al., 1978).

Experimental Part

Investigations on the solubility of NH_4VO_3 in water + ammonia in the given range of the NH_3 concentration varying from 1 mol/dm^3 to 6 mol/dm^3, as a function of temperature, have been carried out.

Drawing the solubility curves of the $NH_4VO_3 + NH_3 + H_2O$ system necessitated carrying out some studies on the equilibrium. The main point of this work was to determine the location of the particular points using the chemical analysis of the solutions.

In six prepared water + ammonia solutions, the concentration of NH_3 was increasing by approximately 1 mol/dm^3. In order to avoid the loss of NH_3, the prepared solutions were stored in bottles tightly closed with rubber caps, equipped with two glass tubes ended with rubber tubes and screw clips. This procedure ensured maintaining practically nonchangeable NH_3 concentrations in the prepared solutions.

The following analytical purity grade compounds were used: NH_4VO_3 (>99%: chloride maximum 0,002%, sulfate maximum 0,005%, phosphate maximum 0,005%; Aldrich Chemical Co. Ltd.) and NH_3 (Nitrogen Works Tarnów-Mościce SA, Poland).

Erlenmeyer flasks, each 100 cm^3 capacity, containing the planned excess of the solid phase and water + ammonia solution of appropriate concentration, were closed with rubber stoppers and placed in a thermostat. For higher NH_3 concentrations, at temperatures 313 K and 323 K, flasks were placed in special metal holders to ensure the proper closure.

The time of thermostating the particular samples was 96 h, being under a constant stirring to ensure complete stabilization of the equilibrium between the solution and the solid phase at the given temperature. The temperature control was done with an accuracy of ±0.1 K.

After the set time limit stirring was stopped and the clear solution was sampled to the Oswald pycnometer, calibrated in the temperature range 293 K to 323 K. After the solution's density was determined, it was taken quantitatively to the graduated flask and the chemical analysis was carried out. The density measurements were performed with an accuracy of ±0.002 g/cm^3.

The concentration of VO_3^- ions was determined by the manganometric method, after reduction with iron(II) (Williams, 1985). The average relative error of the determination was less than 1%. For the smallest concentrations of VO_3^- ions the results were confirmed by spectrophoto-

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Table 1. Solubility of NH_4VO_3 in Water + Ammonia

		c/mol·dm^{-3}			composition of
T/K	ρ/g·cm^{-3}	NH_3 total	NH_4VO_3	NH_3 free	the solid phase
293	1.001	0.050	0.050	0.000	NH_4VO_3
	1.007	1.242	0.146	1.096	NH_4VO_3
	1.002	2.226	0.189	2.037	NH_4VO_3
	0.996	3.206	0.203	3.003	NH_4VO_3
	0.989	4.141	0.197	3.944	NH_4VO_3
	0.980	5.180	0.181	4.999	NH_4VO_3
	0.968	6.420	0.154	6.266	NH_4VO_3
303	1.002	0.074	0.074	0.000	NH_4VO_3
	1.003	1.249	0.156	1.093	NH_4VO_3
	0.998	2.273	0.196	2.077	NH_4VO_3
	0.992	3.228	0.207	3.021	NH_4VO_3
	0.985	4.168	0.201	3.967	NH_4VO_3
	0.976	5.171	0.184	4.987	NH_4VO_3
	0.964	6.406	0.159	6.247	NH_4VO_3
313	1.002	0.105	0.105	0.000	NH_4VO_3
	1.001	1.254	0.168	1.086	NH_4VO_3
	0.996	2.218	0.200	2.018	NH_4VO_3
	0.990	3.180	0.212	2.968	NH_4VO_3
	0.982	4.140	0.206	3.934	NH_4VO_3
	0.974	5.145	0.189	4.956	NH_4VO_3
	0.962	6.359	0.164	6.195	NH_4VO_3
323	1.003	0.147	0.147	0.000	NH_4VO_3
	1.000	1.285	0.185	1.100	NH_4VO_3
	0.994	2.222	0.210	2.012	NH_4VO_3
	0.988	3.155	0.219	2.936	NH_4VO_3
	0.980	4.177	0.212	3.965	NH_4VO_3
	0.972	5.106	0.196	4.910	NH_4VO_3
	0.960	6.416	0.169	6.247	NH_4VO_3

metric analysis, using the method based on the formation the ions colored complex in the reaction with hydrogen peroxide solution (Sandell, 1959). Analyses were conducted using the double beam UV/Vis spectrophotometer (U-2000 Hitachi).

The concentration of the total ammonia was determined by the distillation method with the addition of Devarda's alloy, which protected NH_3 from being oxidized to N_2 under the influence of the VO_3^- ions (Struszyński, 1954), with the average relative error of the determination being less than 1%.

The free ammonia concentration was calculated from the difference between the total ammonia concentration and the concentration of vanadium ions.

The identification of the solid phases being in equilibrium with the solution was performed by both analytical and X-ray methods for some selected points laying on each curve, in the given range of temperatures. The qualitative analysis of precipitates was carried out on an X-ray diffractometer (HZG-4/A-2; GDR) with continuous registration. The X-ray analyses of the solid phases were based on the distribution curves of the dispersed radiation intensity $I = f(\theta)$.

For several points a derivatographic analysis of the precipitate was made in order to confirm additionally the identification of the solid phase. For those measurements an OD-102 apparatus (MOM Hungary) was used, recording both the mass changes of the heated samples and the accompanying energetic effects.

Results and Discussion

The obtained solubility data of NH_4VO_3 in water + ammonia are presented in Table 1. Given are the temperature of the measurement in K, the solution's density in g/cm^3, the concentration each of the components in mol/dm^3, and the solid phase composition.

Data concerning the solubility of NH_4VO_3 in water, as a function of temperature (Trypuć, Kiełkowska, 1996), are also shown in that table.

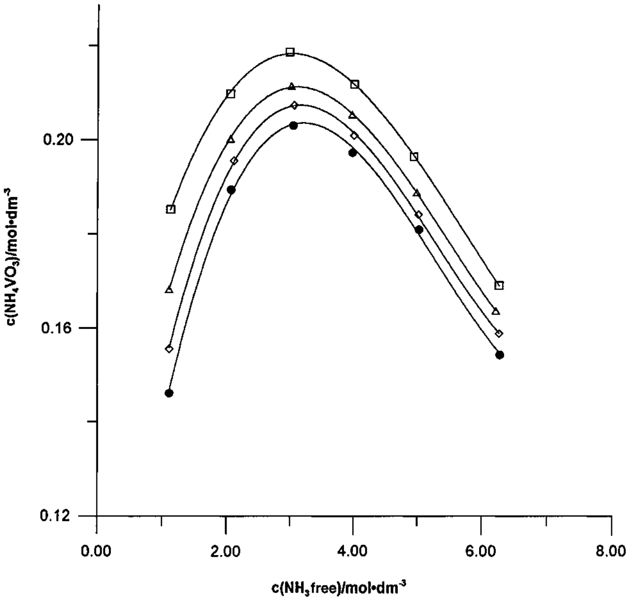

Figure 1. Section of the solubility polytherm of NH_4VO_3 + NH_3 + H_2O system: (●) T = 293 K; (◇) T = 303 K; (△) T = 313 K; (□) T = 323 K.

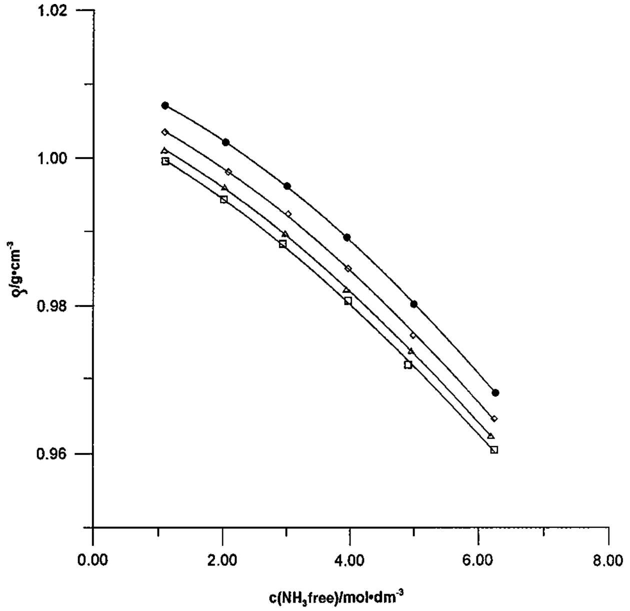

Figure 2. Course of the density changes in dependence on NH_3 concentration and temperature: (●) T = 293 K; (◇) T = 303 K; (△) T = 313 K; (□) T = 323 K.

The section of the solubility curve for the NH_4VO_3 + NH_3 + H_2O system is drawn in Figure 1, and the solution's density dependence on the NH_3 concentration for the given temperatures is shown in Figure 2.

The course of each curve in Figure 1 indicates that with the concentration of NH_3 in the solution increasing steadily to the value of approximately 3 mol/dm^3, the concentration of NH_4VO_3 also systematically increases, which points to the salting effect of NH_3 in this concentration range. At the NH_3 concentration of 3 mol/dm^3, the concentration of NH_4VO_3 reaches its maximum value, and furthermore the increase of NH_3 concentration in the solution results in decreasing NH_4VO_3 concentration, which also proves the salting-out effect of NH_3.

The solubility of NH_4VO_3 in water + ammonia for the given NH_3 concentrations increases with the growth of temperature. From the locations of the particular curves toward each other, it can be concluded that the temperature effect on the solubility of NH_4VO_3 is rather small.

The data presented in Table 1 show the influence of temperature on the solubility of NH_4VO_3 in water + ammonia for constant concentrations of NH_3. The greatest temperature effect on the NH_4VO_3 solubility was observed for those aqueous solutions in the absence of NH_3; the concentration of the salt at $T = 323$ K is 194% higher than that at $T = 293$ K. The presence of NH_3 in the solution causes a considerable decrease of the temperature effect on the solubility of NH_4VO_3. In the case of solutions with the concentration of NH_3 about 1 mol/dm^3, the growth of NH_4VO_3 solubility at $T = 323$ K as compared to that at $T = 293$ K is 27%, for solutions with the concentration of NH_3 about 2 mol/dm^3 it reaches 11%, and for solutions with the concentration of NH_3 above 3 mol/dm ^{3} it is within the range of 8−10%.

The changes of the solution's density, with a slight change of the NH_4VO_3 concentration on temperature, depends mainly on the NH_3 concentration.

As follows from Figure 2, the solution's density apparently decreases with the increasing concentration of NH_3. A similar decrease of density values is also observed with the growth of temperature for the given values of the NH_3 concentration.

Chemical, X-ray, and derivatographic analyses of the examined precipitates revealed that NH_4VO_3 is the solid phase remaining in the equilibrium with the solution.

It should be pointed out that the course of the solubility curve of NH_4VO_3 as a function of NH_3 concentration in the solution cannot be explained by the change of the solid phase composition. Above the 3 mol/dm^3 concentration of NH_3 in the solution, the observed fall of the NH_4VO_3 solubility can account for the common ion effect. For lower NH_3 concentrations, the observed increase of the solubility should be rather associated with the changes in the solution composition. The similar effect of NH_3 on the solubility was reported for NH_4Cl at 288.5 K (Pelsh, 1969).

In the case of the NaCl + NH_3 + H_2O (Trypuć, 1987) and KCl + NH_3 + H_2O (Koneczny et al., 1973) systems, this salting-out effect of NH_3 was observed for the entire range of studied concentrations.

On the basis of the literature review it is not quite possible to explain exactly this alternating effect of NH_3 on the solubility of various salts.

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